AIP Applied Physics Letters

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Citation: Applied Physics Letters **103**, 192907 (2013); doi: 10.1063/1.4829150

View online: http://dx.doi.org/10.1063/1.4829150

View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/103/19?ver=pdfcov

Published by the AIP Publishing

Fatigue-free unipolar strain behavior in $CaZrO_3$ and MnO_2 co-modified $(K,Na)NbO_3$-based lead-free piezoceramics

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(Received 21 September 2013; accepted 19 October 2013; published online 5 November 2013)

The unipolar fatigue behavior of $CaZrO_3$ and MnO_2 co-modified (K,Na,Li)(Nb,Ta)O_3 lead-free piezoceramics was investigated systematically. The well-known charge agglomeration model is shown to explain the overall changes observed during unipolar fatigue, such as the development of bias field as well as the anisotropy in bipolar strain hysteresis and field-dependent dielectric permittivity. In addition, it is found that the unipolar strain exhibits only small degradation within 3% at the field amplitude of 2 kV/mm up to 10^7 cycles. This exceptionally good fatigue resistance is identified due to the presence of additional process, assigned as a "softening" effect that competes against the usual fatigue effect.
[http://dx.doi.org/10.1063/1.4829150]

$(K,Na)NbO_3$-based (denoted by KNN) lead-free piezoceramics have been the spotlight in the search for practically viable substitutes for the hazardous Pb(Zr,Ti)O_3 (PZT) family, particularly in applications of actuators and high precision positioning devices.[1–3] A drawback of this class of materials is the occurrence of a polymorphic phase transition (PPT) around room temperature, which renders the piezoelectric properties very sensitive to temperature. To improve the general piezoelectric performance and the temperature stability of KNN ceramics, various attempts through manipulation of crystallographic structure[4,5] or refined processing techniques[6] have been published. Especially, $CaZrO_3$ and MnO_2 co-modified (K,Na,Li)(Nb,Ta)O_3 (CZ5) lead-free piezoceramics have high potential, since they show a large normalized strain d_{33}* of 300–350 pm/V, which is extremely stable in the temperature range from room temperature up to 175 °C.[7] However, practical applications demand not only outstanding piezoelectric properties but also the reliability and long term stability during cyclic electric loading to ensure successful industrial implementation.[8]

The most common electric loading scenario for piezoelectric elements in actuator applications is the unipolar driving mode, where an electric signal is cycled between zero and a maximum field without reversing polarity. Long-term unipolar cycling is known to induce fatigue effects, which can result, e.g., in the reduction of unipolar strain and polarization or in the appearance of an internal bias field (E_{bias}).[8,9] For the PZT family, many fatigue studies can be found in the literature.[10–13] One of the most accepted mechanisms explaining unipolar fatigue behavior of PZT ceramics is a charge agglomeration model, embodied by the redistribution of charge carriers during cycling and their agglomeration at the grain boundaries and internal defects.[9,14–17] However, recent fatigue studies on newly developed lead-free ceramics have revealed that the models commonly used to describe fatigue in PZT-based systems do not always fit.[18,19] Therefore, it is necessary to carefully investigate the fatigue characteristics of promising lead-free compositions. Especially, only a few fatigue studies have been published so far for KNN-based materials,[20–23] and a detailed understanding of the unipolar fatigue mechanism, which is crucial for further improving the unipolar fatigue resistance, is still missing.

In the present work, the unipolar fatigue behavior of CZ5 piezoceramics was investigated. It was found that the CZ5 ceramics show an excellent unipolar fatigue resistance comparable to that of a commercial soft PZT. The unipolar strain of CZ5 ceramics does not show discernable degradation up to 10^7 cycles, which combined with the good piezoelectric properties and the temperature stability makes this system a promising candidate for actuator applications. Prior work on Mn-doped KNN revealed that the conductivity minimum between electron and electron hole conductivity can be established using Mn-doping and annealing.[24] Thus, the mild fatigue behavior observed may be attributed to the low conductivity leading to only moderate charge carrier agglomeration at the grain boundaries.

The CZ5 ceramics were prepared via a conventional solid state method as described elsewhere.[7] The as-sintered CZ5 ceramics were ground to 1 mm in thickness and 7 mm in diameter and the surfaces were polished with diamond paste down to 1 μm. It is well accepted that the quality of electrode-surface contact has a significant effect on the evolution of fatigue behavior.[9] To guarantee good interface contact, approximately 50 nm of a Ag layer was deposited onto both sides of the samples by sputtering. Additionally, Ag paste was painted onto the deposited Ag layers and fired at 550 °C for 30 min to protect the electrode from scratches. The samples were fatigued with a positive unipolar sinusoidal electric signal with the amplitude of 2 kV/mm (which corresponds to about two times of the coercive field, E_C) at 50 Hz up to 10^7 cycles. No prepoling treatment was carried

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out before the first measurement. For selected decades of cycles, the fatigue process was stopped, and the large signal parameters polarization P_3 and strain S_{33} as well as small signal parameters piezoelectric constant d_{33} and permittivity ε_{33} were measured. It should be mentioned that tensor notation, e.g., S_{33}, is used in the present study. The large signal hysteresis for P_3 and S_{33} were determined with the maximum field amplitude of 4 kV/mm at the frequency of 1 Hz. The small-signal field-dependent d_{33} and ε_{33} were measured by applying a triangular signal of 4 kV/mm and the frequency of 1 Hz, on which an AC voltage of 25 V and at 250 Hz was superimposed. Unipolar strain hysteresis was obtained with a unipolar triangular signal of 4 kV/mm at 1 Hz. The aforementioned fatigue and measurements were performed using the aixACCT TF Analyzer 1000 (aixACCT Systems GmbH, Germany). To investigate the effect of thermal treatment on fatigue behavior, the fatigued ceramics were annealed at 500 °C for 4 h, after which the properties were also characterized.

Suitable materials for piezoelectric applications not only show high piezoelectric properties but also have to be reliable under long-term electric cycling. For electromechanical applications such as sensors or ultrasonic devices, a high piezoelectric coefficient d_{33} is often the desired quality. For actuator applications, however, the normalized strain ($d_{33}{*} = S_{max}/E_{max}$) is a more important feature.[6,7,25] For KNN-based materials this property and its fatigue behavior did not get much attention so far,[21,23] even though it is a crucial aspect for industrial implementation.

Unipolar S_{33}-E_3 curves before and after distinct unipolar fatigue cycles are displayed in Fig. 1(a), showing no distinct variation during the fatigue process. Figure 1(b) depicts the change of strain deduced from the unipolar S_{33}-E_3 curves in Fig. 1(a). To set the fatigue behavior of CZ5 in relation to the degradation characteristics of PZT under the same cycling conditions, the same parameters of a commercial soft PZT with the composition $Pb_{0.99}[Zr_{0.45}Ti_{0.47}(Ni_{0.33}Sb_{0.67})_{0.08}]O_3$ (PIC151 from PI Ceramics, Lederhose, Germany) showing a similar coercive field E_C as the CZ5 ceramics are given as well (data extracted from Ref. 9). The strain of CZ5 shows a peak around 10^6 cycles, but the general variation of the strain up to 10^7 cycles is within $\pm 3\%$ of original value. In contrast to that, PIC151 experiences approximately 15% reduction in strain behavior after 10^7 electric cycles, though it can retrieve almost fatigue-free state of about 4% loss to the original value approaching to 3×10^7 cycles. This clearly demonstrates that CZ5 ceramics exhibit fatigue-free unipolar strain behavior. Moreover, it should be noted that CZ5 exhibits much better fatigue resistance than other KNN-based materials.[21,26] For the BNT-BT based materials, both low[27] as well as high[18] fatigue resistance can be obtained.

To understand the behavior of the unipolar strain during electrical cycling more in detail, bipolar hysteresis loops of polarization P_3, strain S_{33}, permittivity ε_{33} and piezoelectric coefficient d_{33} were recorded in the unfatigued state and after distinct cycling steps. The evolution of both large signal (polarization P_3 and strain S_{33}) hysteresis and small signal (piezoelectric coefficient d_{33} and permittivity ε_{33}) curves with unipolar electric cycling is displayed in Fig. 2. It should be mentioned that the large and small signal loops displayed

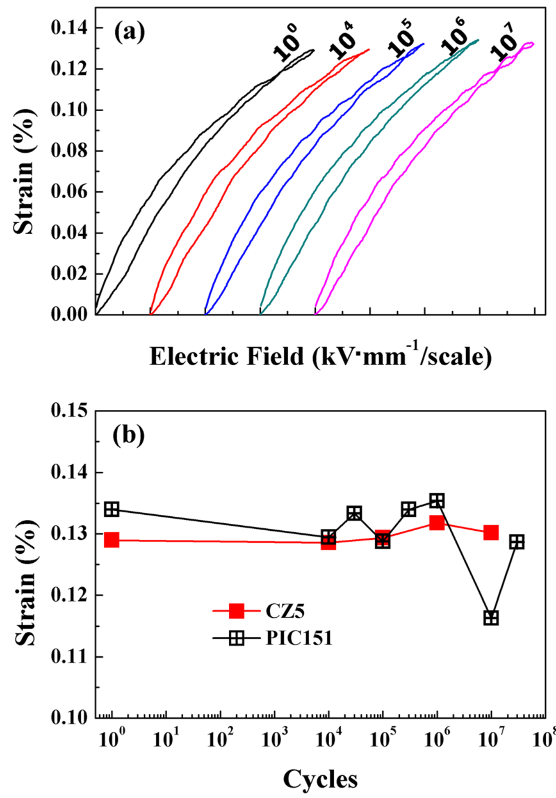

FIG. 1. (a) Unipolar S_{33}-E_3 curves of CZ5 ceramics before and after 10^4, 10^5, 10^6, and 10^7 unipolar fatigue cycles, (b) strain of CZ5 ceramics as a function of cycles with the data of a soft commercial PZT (PIC151) provided for comparison.[9]

for the unfatigued state are effectively the third and fourth bipolar electric cycle applied to the sample, respectively. It can be seen that unipolar cycling does not lead to obvious changes in the polarization hysteresis up to 10^7 cycles (Fig. 2(a) and S1).[28] However, the piezoelectric coefficient (Fig. 2(b)) shows a slight shift along the positive ordinate, while strain and permittivity loops (Figs. 2(c) and 2(d), respectively) develop an asymmetric shape. To illustrate the development of the fatigue behavior, characteristic parameters were extracted from Fig. 2 and plotted vs. cycle number in Figs. 3 and 4.

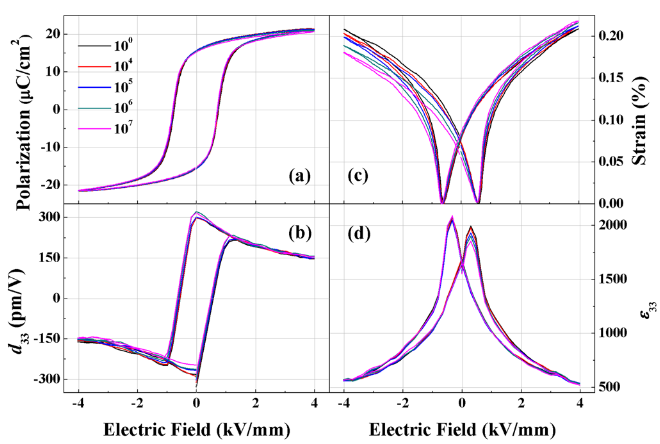

FIG. 2. (a) P_3-E_3, (b) d_{33}-E_3, (c) S_{33}-E_3, and (d) ε_{33}-E_3 of CZ5 ceramics before and after 10^4, 10^5, 10^6, and 10^7 unipolar fatigue cycles.

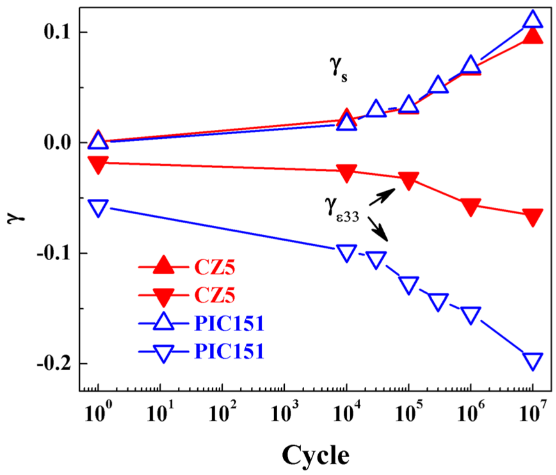

FIG. 3. Asymmetry factors γ_s and $\gamma_{\varepsilon 33}$ (refer to Eqs. (1) and (2) for the definition) as a function of unipolar fatigue cycle number. The data of PIC151 ceramics were presented for comparison.[9]

The asymmetries developed in the strain S_{33}-E_3 and permittivity ε_{33}-E_3 loops can be quantified using asymmetry factors γ_s and $\gamma_{\varepsilon 33}$ in Eqs. (1) and (2), respectively,[9]

$$\gamma_s = \frac{\Delta S_{33}^{+} - \Delta S_{33}^{-}}{\Delta S_{33}^{+} + \Delta S_{33}^{-}}, \tag{1}$$

$$\gamma_{\varepsilon_{33}} = \frac{\Delta \varepsilon_{33}^{+} - \Delta \varepsilon_{33}^{-}}{\Delta \varepsilon_{33}^{+} + \Delta \varepsilon_{33}^{-}}. \tag{2}$$

The corresponding values together with data for the PIC151 ceramic are given in Fig. 3. As the asymmetries are relative values already, no normalization on the unfatigued values was done. The data show that the strain asymmetry vs. cycle number for both materials is comparable, whereas the CZ5 material develops significantly less asymmetry in the permittivity as compared to PIC151. Overall, these results indicate that the unipolar fatigue resistance of CZ5 is comparable to that of PIC151.

The plots shown in Fig. 4 deliver innovative and inspiring information, which in general indicates that unipolar cycling induces a competition between softening and fatigue effects. It is known that an internal bias field (E_{bias}) can develop with unipolar cycling, which can be extracted from either the P_3-E_3 or the d_{33}-E_3 curve. However, since polarization measurement is a relative method, it is more reasonable to define E_{bias} as follows:

$$E_{bias} = -\frac{E_{C+} + E_{C-}}{2}, \tag{3}$$

where the E_{C+} and E_{C-} are the positive and negative coercive field in d_{33}-E_3 curves, respectively. The softening effect, which resembles consequence of the poling process, can be inferred from the improvement of $2P_r$ and small signal d_{33} (up to 10^6 cycles), which is a consequence of enhanced domain wall mobility, while the fatigue effect dominates after 10^6 cycles, leading to a decrease of the various parameters. It is observed that the fatigue effect is well in accordance with the development of E_{bias}. However, the situation for negative strain (S_{neg}, the difference between the remanent and

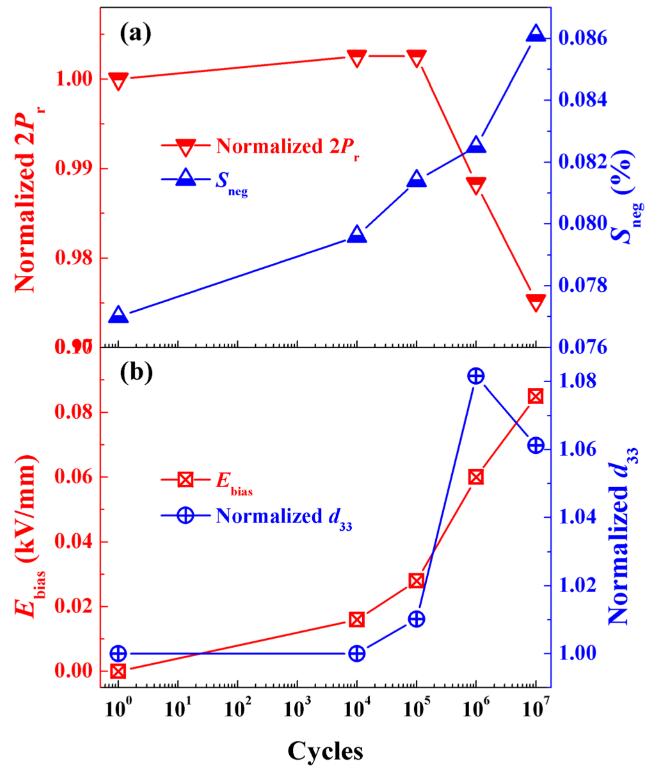

FIG. 4. Unipolar fatigue characteristics in terms of (a) normalized switchable polarization $2P_r$ and S_{neg}, (b) internal bias field E_{bias} and normalized piezoelectric coefficient d_{33}.

minimum strain in bipolar strain curve) is more complicated. Although an increase of S_{neg} is normally considered to occur due to the softening effect, which is normally related to improved domain wall mobility, the asymmetry developing in the bipolar strain curve also contributes to the increase of S_{neg} in the current study.

As the unipolar fatigue characteristics of CZ5 and PIC151 ceramics appear to develop in a comparable fashion, a similar mechanism might be responsible for the degradation in both materials. For PZT materials, a model based on charge carrier agglomeration has been used to describe the unipolar fatigue mechanism,[9,16] which can be successfully employed to describe the unipolar fatigue behavior in CZ5, as shown in Fig. 5. During electrical cycling, the polarization state in each domain changes continuously. At grain boundaries, the polarization vectors of domains in neighboring grains can not compensate each other due to crystallographic mismatch, as exemplified in Fig. 5(a). This leads to the occurrence of strong, locally varying depolarization fields (denoted by σ^+ and σ^-). Free charge carriers in the vicinity will be re-distributed to compensate the local depolarization

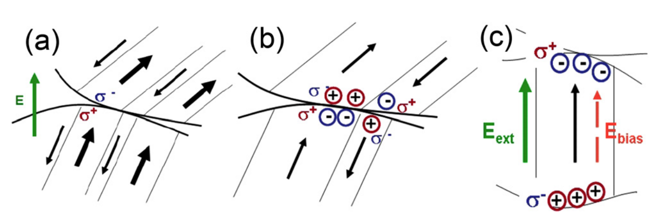

FIG. 5. Illustration of charge carrier agglomeration near the grain boundary during the fatigue process.

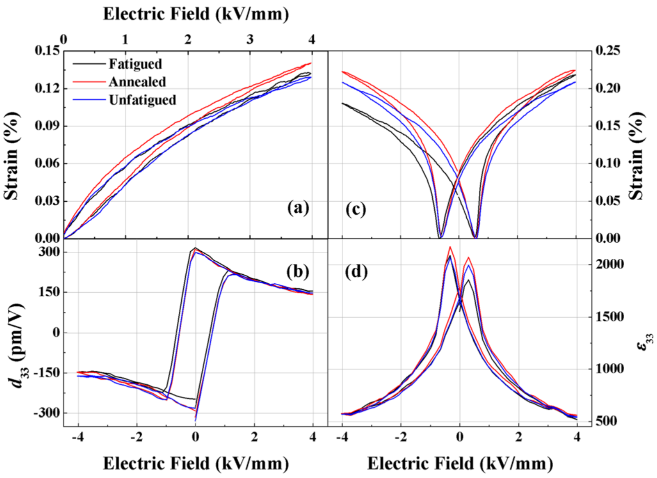

FIG. 6. Effect of thermal annealing on (a) unipolar S_{33}-E_3, (b) d_{33}-E_3, (c) S_{33}-E_3, and (d) ε_{33}-E_3 of 5CZ ceramics compared to the ones of unfatigued and fatigued states.

fields (see Fig. 5(b)). This agglomeration of charges forms a local bias field E_{bias}, which has the same orientation as the cycling field (Fig. 5(c)). The superposition of all local bias fields leads to the macroscopically observable shift of the hysteresis loops and can be seen as the source for the degradation characteristics in CZ5 such as the asymmetries in strain and permittivity.

In addition to the agglomeration of free charges being the source of fatigue in piezoelectric ceramics, mechanical deterioration due to cycling has to be taken into account as well. It was reported that for both bipolar[29] and unipolar[15] fatigued PZT ceramics, the piezoelectric performance can at least partially be recovered through a simple thermal annealing process, as long as no mechanical degradation such as development of cracks or electrode delamination has occurred. Therefore, the stability of the induced degradation against thermal treatment was tested. The unipolar strain curves, as well as bipolar large signal and small signal curves of unfatigued, fatigued and annealed CZ5 ceramics were shown in Fig. 6 (due to space limit, the polarization comparison is shown in Fig. S2).[28] It can be seen that the thermal annealing treatment leads to full recovery of the fatigued properties of CZ5 ceramics, indicating that no mechanical deterioration was induced during the unipolar cycling process.

In summary, the unipolar fatigue behavior of KNN-based ceramics has been investigated systematically. It was found that the general fatigue characteristics develop similar to PZT-based materials and the electrical properties can be fully recovered after annealing treatment, indicating that no mechanical deterioration occurs during the unipolar cycling process. While a charge agglomeration model can describe the unipolar fatigue behavior, the current study reveals an interesting competition between softening and fatigue effects. The superior fatigue characteristics compared to other lead-free materials might be due to the reduced conductivity caused by Mn-doping. More importantly, the unipolar strain does not degrade up to 10^7 unipolar cycles, rendering this material promising for actuator applications.

This work was supported by National Nature Science Foundation of China (Grant No. 51332002, 51302144, 51221291, and 51211140345) and the Ministry of Science and Technology of China under the Grant No. 2009CB623304. K.W. acknowledges the Alexander von Humboldt foundation for a fellowship. J.G. acknowledges support from the Australian Research Council (Grant No. DE120102644).

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[28]See supplementary material at http://dx.doi.org/10.1063/1.4829150 for enlarged P_3-E_3 loops of CZ5 ceramics recorded before and after certain unipolar fatigue cycles and for P_3-E_3 loops of CZ5 ceramics for unfatigued, fatigued and annealed states.
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